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# Controlled reduction for size selective synthesis of thiolate-protected gold nanoclusters $\text{Au}_n$ ( $n = 20, 24, 39, 40$ )

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## Abstract

This work presents a controlled reduction method for the selective synthesis of different sized gold nanoclusters protected by thiolate ( $\text{SR} = \text{SC}_2\text{H}_4\text{Ph}$ ). Starting with  $\text{Au}(\text{III})$  salt, all the syntheses of  $\text{Au}_n(\text{SR})_m$  nanoclusters with  $(n, m) = (20, 16), (24, 20), (39, 29)$ , and  $(40, 30)$  necessitate experimental conditions of slow stirring and slow reduction of  $\text{Au}(\text{I})$  intermediate species. By controlling the reaction kinetics for the reduction of  $\text{Au}(\text{I})$  into clusters by  $\text{NaBH}_4$ , different sized gold nanoclusters are selectively obtained. Two factors are identified to be important for the selective growth of  $\text{Au}_{20}$ ,  $\text{Au}_{24}$ , and  $\text{Au}_{39/40}$  nanoclusters, including the stirring speed of the  $\text{Au}(\text{I})$  solution and the  $\text{NaBH}_4$  addition speed during the step of  $\text{Au}(\text{I})$  reduction to clusters. When comparing with the synthesis of  $\text{Au}_{25}(\text{SC}_2\text{H}_4\text{Ph})_{18}$  nanoclusters, we further identified that the reduction degree of  $\text{Au}(\text{I})$  by  $\text{NaBH}_4$  also plays an important role in controlling cluster size. Overall, our results demonstrate the feasibility of attaining new sizes of gold nanoclusters via a controlled reduction route.

**Keywords:** Gold nanoclusters, Size selective synthesis, Controlled reduction

## Background

Gold nanoclusters [1-6] have received extensive attention owing to their interesting optical properties [6-9], magnetism [10,11], fluorescence [12-16], chirality [17-20], redox properties [21-27], as well as potential applications in many fields such as catalysis and biological labeling [28-33]. The new physicochemical properties of gold nanoclusters are largely imparted by the discrete electronic structure of the metal core due to quantum confinement effects. The surface of the cluster may also influence some of the material properties, such as chirality [18,19].

Recently, major advances in wet chemical synthesis of nanoclusters have been achieved, and it has been possible to control nanoclusters at the atomic level. A number of well-defined nanoclusters have been reported; however, only a few can be obtained in bulk quantities and in high yields via facile synthetic methods [34].

Among the various thiolate-protected gold nanoclusters,  $\text{Au}_{25}(\text{SR})_{18}$  has been extensively studied [21-27,35-41]. Other well-defined nanoclusters have also been attained, such as  $\text{Au}_{36}$  [42],  $\text{Au}_{38}$  [43,44],  $\text{Au}_{102}$  [45], and  $\text{Au}_{144}$  [46,47].

We previously reported a kinetically controlled synthetic approach for the synthesis of highly pure  $\text{Au}_{25}(\text{SR})_{18}$  nanoclusters [48,49]. The method involves a size focusing mechanism, that is, the initial cluster product of mixed sizes is converged to a specific size of highest stability under appropriate conditions [34]. By controlling the size range of the initial nanoclusters, one can achieve atomic monodispersity of nanoclusters [34]. This synthetic approach constitutes a versatile strategy for gold nanocluster synthesis [49] and has been demonstrated in the synthesis of quite a number of atomically precise  $\text{Au}_n(\text{SR})_m$  nanoclusters, such as  $\text{Au}_{25}$ ,  $\text{Au}_{38}$ , and  $\text{Au}_{144}$  [34].

Herein, we demonstrate that a controlled reduction method can lead to different sizes of gold nanoclusters. By making a modification of the synthetic method of  $\text{Au}_{24}$  nanoclusters [50], we have obtained two new sizes, including  $\text{Au}_{39}(\text{SC}_2\text{H}_4\text{Ph})_{29}$  and  $\text{Au}_{40}(\text{SC}_2\text{H}_4\text{Ph})_{30}$ . Our

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results explicitly show that the initial growth stage of nanoclusters is critical and can be largely influenced by experimental conditions. This method of controlled reduction has expanded the synthetic approaches for preparing nanoclusters with size control.

## Methods

### Materials

The following chemicals were used: tetrachloroauric(III) acid ( $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ , >99.99% metals basis, Sigma-Aldrich Corporation, St. Louis, MO, USA), tetraoctylammonium bromide (TOAB, ≥98%, Fluka Chemicals Limited, Gillingham, Medway, UK), phenylethanethiol ( $\text{PhC}_2\text{H}_4\text{SH}$ , 99%, Acros Organics, Thermo Fisher Scientific, NJ, USA), and sodium borohydride (99.99%, metals basis, Sigma-Aldrich). The solvents include toluene (HPLC grade, ≥99.9%, Sigma-Aldrich), ethanol (absolute, 200 proof, PHARMCO-AAPER, Shelbyville, KY, USA). Pure water was from Wahaha Co. LTD (Hangzhou, China). All glassware was thoroughly cleaned with *aqua regia* ( $\text{HCl} : \text{HNO}_3 = 3:1$  vol), rinsed with copious pure water, and then dried in an oven prior to use.

### Analysis tools

All UV-visible (vis) absorption spectra of Au nanoclusters in either toluene or methylene chloride were recorded using a Hewlett-Packard (HP, Palo Alto, CA, USA) 8453 diode array spectrophotometer. Electrospray ionization mass spectra were acquired using a Waters Q-TOF (Waters Corporation, Milford, MA, USA) mass spectrometer equipped with a Z-spray source. The sample solution (approximately 1 mg/mL) dissolved in toluene was diluted in dry methanol (50 mM cesium acetate  $\text{CsAc}$ , 1:2 vol). The sample was directly infused at 5  $\mu\text{L}/\text{min}$ . The source temperature was kept at 70°C. The spray voltage was kept at 2.20 kV; the cone voltage, at 60 V.

### Synthesis of $\text{Au}_n$ nanoclusters ( $n = 39$ and 40)

$\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$  (0.1612 g, 0.41 mmol) was dissolved in 5 mL water, and tetraoctylammonium bromide (TOAB, 0.2541 g, 0.465 mmol) was dissolved in 10 mL toluene. These two solutions were combined in a 25-mL tri-neck, round-bottom flask. The solution was vigorously stirred (approximately 1,100 rpm) with a magnetic stir bar to facilitate phase transfer of Au(III) salt into the toluene phase. After approximately 15 min, phase transfer was completed; the clear aqueous phase was then removed. The toluene solution was cooled down to 0°C in an ice bath over a period of approximately 30 min under constant magnetic stirring. After that, magnetic stirring was reduced to a slow speed (approximately 100 rpm),  $\text{PhC}_2\text{H}_4\text{SH}$  (0.20 mL, approximately threefold the moles of gold) was added, and the solution was kept under slow stirring. The solution color changed slowly from deep red

to faint yellow and to colorless over approximately 1 h. After that, the speed of magnetic stirring was increased from approximately 100 to 400 rpm. At the same time, 1 mL aqueous solution of  $\text{NaBH}_4$  (0.44 mol/L, freshly made with ice-cold water) was dropwise added to the toluene solution over a 15-min period using a 1-mL syringe. The color of the solution turned black gradually. After the dropwise addition of  $\text{NaBH}_4$ , the reaction was allowed to further proceed overnight. The optical absorption spectrum of the crude reaction product (diluted with toluene) shows a distinct absorption band at approximately 800 nm.

### Post-synthetic treatment of the crude product

The aqueous layer at the bottom of the flask was removed using a syringe, and the toluene solution was concentrated by rotary evaporation at room temperature. Ethanol (approximately 50 mL) was added to precipitate the Au nanoclusters. The brown, turbid solution was allowed to stand on bench for several hours. The precipitate was collected and redissolved in toluene. This precipitation/dissolution process was repeated with ethanol. The crude mixture was extracted with methylene chloride/acetonitrile (1:9 vol) to remove a small amount of  $\text{Au}_{20}(\text{SC}_2\text{H}_4\text{Ph})_{16}$  (its optical absorption band at approximately 485 nm) [51]. After  $\text{Au}_{20}$  was removed from the product,  $\text{Au}_{24}(\text{SC}_2\text{H}_4\text{Ph})_{20}$  nanoclusters were removed by a second extraction with methylene chloride/acetonitrile (1:2 vol) [50]. The final remaining product was collected and characterized by mass spectrometry.

## Results and discussion

### Identification of $\text{Au}_{39}(\text{SC}_2\text{H}_4\text{Ph})_{29}$ and $\text{Au}_{40}(\text{SC}_2\text{H}_4\text{Ph})_{30}$

Starting with an Au(III) salt precursor, the synthesis of gold nanoclusters involves two primary stages: (a) reduction of Au(III) to Au(I) by HSR, during which the formed Au(I) intermediate species spontaneously aggregates into polymeric Au(I) species (unknown structure), and (b) reduction of Au(I) to  $\text{Au}_n(\text{SR})_m$  nanoclusters by  $\text{NaBH}_4$ .

In this work, we have identified several important factors for the synthesis of nanoclusters  $\text{Au}_{39}$  and  $\text{Au}_{40}$ , including the stirring speed of the reaction mixture, the addition speed, and the amount of  $\text{NaBH}_4$  solution to reduce Au(I) into clusters. The synthetic conditions reported in this work differ from the previous syntheses of  $\text{Au}_{19}(\text{SC}_2\text{H}_4\text{Ph})_{13}$ ,  $\text{Au}_{20}(\text{SC}_2\text{H}_4\text{Ph})_{16}$  and  $\text{Au}_{24}(\text{SC}_2\text{H}_4\text{Ph})_{20}$  (see 'Methods' section) [50-52]. Specifically, in the present work, our major modification lies in the *stirring speed* of the Au(I) intermediate solution when reduced by  $\text{NaBH}_4$ . In a previous work,  $\text{Au}_{20}(\text{SC}_2\text{H}_4\text{Ph})_{16}$  and  $\text{Au}_{24}(\text{SC}_2\text{H}_4\text{Ph})_{20}$  were synthesized by controlling the stirring speed for the reduction step of Au(I) by  $\text{NaBH}_4$  for example, approximately 50 rpm for

$\text{Au}_{20}(\text{SC}_2\text{H}_4\text{Ph})_{16}$  and approximately 100 rpm for  $\text{Au}_{24}(\text{SC}_2\text{H}_4\text{Ph})_{20}$ .

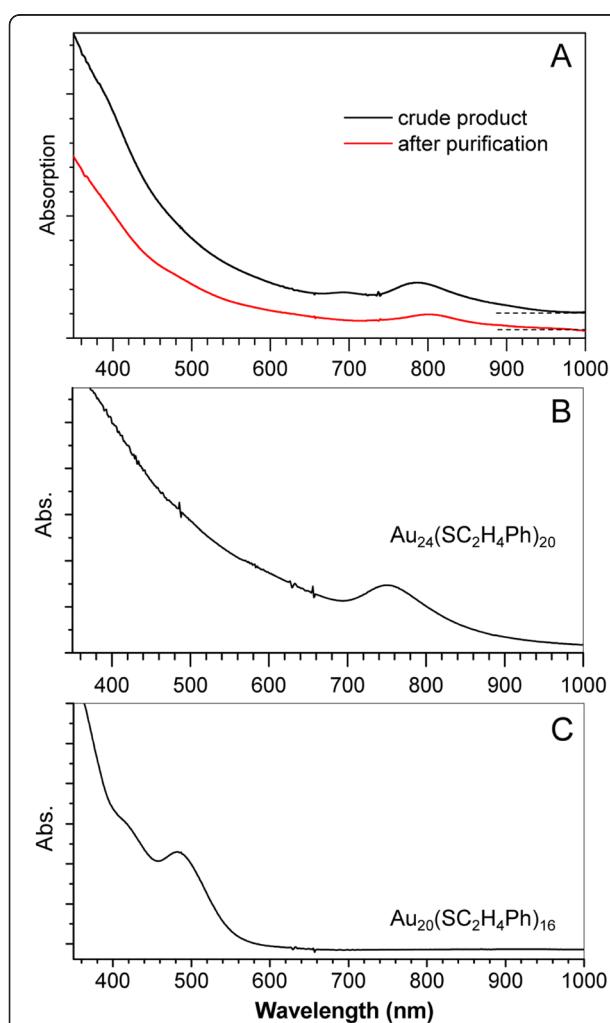
To synthesize larger-sized nanoclusters, we rationalize that the kinetics of the reduction reaction of Au(I) intermediate species by  $\text{NaBH}_4$  may be important for potential size control. Motivated by that, we systematically varied the synthetic conditions and also compared with the typical method for  $\text{Au}_{25}(\text{SC}_2\text{H}_4\text{Ph})_{18}$  synthesis. Interestingly, we found that with the stirring speed being increased to approximately 400 rpm, the crude product (Figure 1A) shows an optical spectrum different from that of  $\text{Au}_{24}(\text{SC}_2\text{H}_4\text{Ph})_{20}$  or  $\text{Au}_{20}(\text{SC}_2\text{H}_4\text{Ph})_{16}$  (Figure 1B,C). A new absorption peak centered at approximately 800 nm was observed (Figure 1A), indicating that some new species have been formed in this controlled reduction process. Of note, the small peak at approximately 700 nm (Figure 1A) is due to the concurrent formation of a small amount of  $\text{Au}_{24}(\text{SC}_2\text{H}_4\text{Ph})_{20}$

clusters as impurities in the synthesis of the new clusters. To remove  $\text{Au}_{24}$  and possible  $\text{Au}_{20}$  impurities from the product, the clusters in the crude product were precipitated by adding ethanol, and the crude product was then extracted with  $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{CN}$  (1:9 vol) to selectively dissolve  $\text{Au}_{20}(\text{SC}_2\text{H}_4\text{Ph})_{16}$  from the product. The remained undissolved produce was followed by a second extraction with  $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{CN}$  (1:2 vol) to remove  $\text{Au}_{24}(\text{SC}_2\text{H}_4\text{Ph})_{20}$ . The final remaining product is largely free of  $\text{Au}_{24}$  and  $\text{Au}_{20}$  impurities, as evidenced in the disappearance of the 700-nm band in the optical spectrum (Figure 1A, red profile). The relatively pure product is subject to further characterization for cluster formula determination.

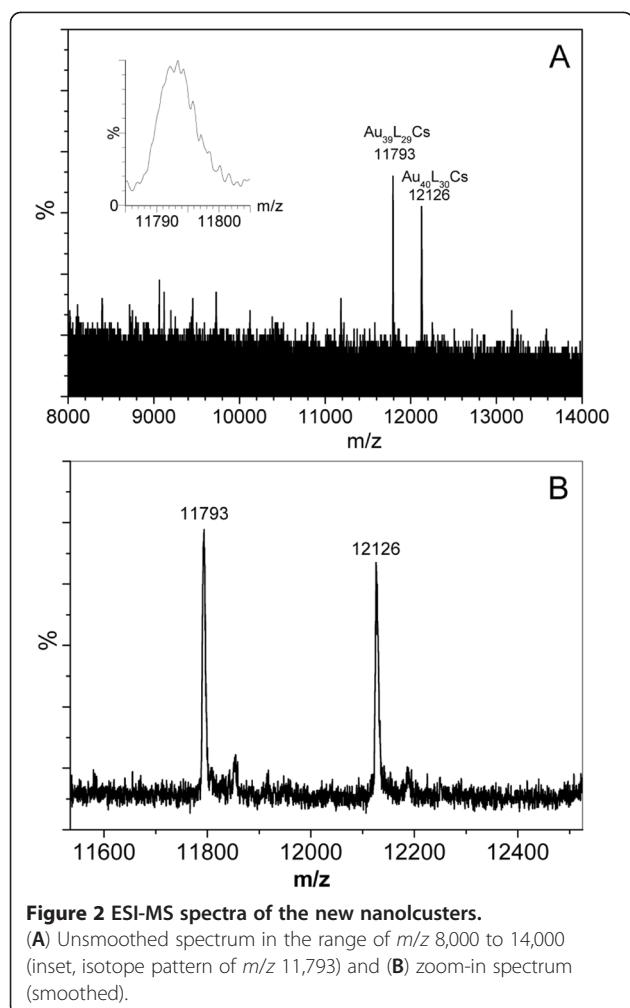
We employ electrospray ionization mass spectrometry (ESI-MS) to determine the composition of the new gold cluster product. A solution of cesium acetate ( $\text{CsAc}$ , 50 mM, in dry methanol) was added to a toluene solution of gold clusters at 1:1 or 1:2 (vol). ESI-MS detects the cluster-Cs adducts that are positively charged due to  $\text{Cs}^+$  addition to the cluster surface.

The low-mass portion of the spectrum consists of all  $[\text{CsAc}]_x\text{Cs}^+$  signals (Figure S1 in Additional file 1), and residual  $\text{Au}_{24}(\text{SC}_2\text{H}_4\text{Ph})_{20}\text{Cs}$  was also observed at  $m/z$  7,603 (calculated FW = 7604 for mono-Cs adduct). The high-mass portion (Figure 2) shows two peaks at  $m/z$  11,793 and 12,127 (Figure 2A, unsmoothed spectrum; Figure 2B, smoothed). These two signals are corresponding to the new clusters formed in the controlled reduction process. Both peaks indicate +1 ions, evidenced by the unity spacing of the isotope-resolved peaks (see Figure 2A inset, for  $m/z$  11,793). After subtracting one  $\text{Cs}^+$  ion (FW = 133), the masses of the two new clusters are determined to be 11,660 and 11,994 Da. Unfortunately, isolation of these two mixed clusters into pure ones has not been successful so far.

To deduce the formulas of the two new  $\text{Au}_n(\text{SC}_2\text{H}_4\text{Ph})_m$  clusters based upon the ESI-MS data, we first determine the minimum value of the gold atom number ( $n$ ), which corresponds to the limiting case of Au(I):SR complexes, i.e., when  $n=m$ . This gives rise to 11,660/337 approximately 35 for the peak of  $m/z$  11,660. We then construct candidate formulas by systematically increasing  $n$  starting from 35. For example, for  $n=36$ , we list two closest matches to the ESI-determined mass of 11,660 Da, one with the smallest negative deviation, i.e.,  $(n, m)=(36, 33)$ , and the other with the smallest positive deviation, i.e.,  $(n, m)=(36, 34)$ , see Table 1; note that other  $m$  values for  $n=36$  are not pursued since they deviate more from the ESI mass of 11,660 Da. Following this method, one can list all the possible formulas until the limiting case of 11,660 Da consisting of all gold atoms, which is the upper limiting case since a certain number of thiolate ligands must be present to



**Figure 1** UV-vis absorption spectra. (A) The new cluster product (black profile, crude product without any extraction; red, after two extractions), (B) pure  $\text{Au}_{24}(\text{SC}_2\text{H}_4\text{Ph})_{20}$ , and (C) pure  $\text{Au}_{20}(\text{SC}_2\text{H}_4\text{Ph})_{16}$ .



**Figure 2** ESI-MS spectra of the new nanoclusters.

(A) Unsmoothed spectrum in the range of  $m/z$  8,000 to 14,000 (inset, isotope pattern of  $m/z$  11,793) and (B) zoom-in spectrum (smoothed).

protect the metal core. By comparing the candidate formulas with the ESI-MS-determined precise mass of 11,660 Da, we readily obtain the  $\text{Au}_{39}(\text{SC}_2\text{H}_4\text{Ph})_{29}$  formula (calculated FW = 11661; deviation, 1 Da), as reflected in Table 1. Similarly, the cluster of 11,993 Da is determined to be  $\text{Au}_{40}(\text{SC}_2\text{H}_4\text{Ph})_{30}$  (calculated FW = 11,995; deviation, 2 Da). A deviation of 0.5 to 2 Da is reasonable at this high mass range.

#### Insight into the size-controlled synthesis of $\text{Au}_{39/40}$ nanoclusters

The attainment of two new nanoclusters,  $\text{Au}_{39}(\text{SC}_2\text{H}_4\text{Ph})_{29}$  and  $\text{Au}_{40}(\text{SC}_2\text{H}_4\text{Ph})_{30}$ , demonstrates the feasibility of controlling cluster size via controlled reduction. Herein, we discuss some insights obtained regarding the synthetic processes of  $\text{Au}_{20}$ ,  $\text{Au}_{24}$ , and  $\text{Au}_{39/40}$ . These four cluster species belong to a new series, as  $\text{Au}_{20}$  and  $\text{Au}_{24}$  are formed concurrently, albeit in small amounts, in the synthesis of  $\text{Au}_{39/40}$  nanoclusters. However, by controlling the reaction process, one may selectively produce  $\text{Au}_{20}$ ,  $\text{Au}_{24}$ , or  $\text{Au}_{39/40}$ . When using Au(III) as the starting material for

**Table 1** List of candidate formulas for the two clusters

$(n, m)$ Candidate formulas for $m/z$ 11,660			$(n, m)$ Candidate formulas for $m/z$ 11,993		
Formula	Mass	Deviation from 11,660 Da	Formula	Mass	Deviation from 11,993 Da
(35, 35)	11696.3	+36.3	(36, 36)	12030.5	+37.5
(36, 33)	11618.8	-41.2	(37, 34)	11952.9	-40.1
(36, 34)	11756.0	+90.0	(37, 35)	12090.2	+97.2
(37, 31)	11541.3	-118.7	(38, 32)	11875.5	-117.5
(37, 32)	11678.5	+18.5	(38, 33)	12012.7	+19.7
(38, 30)	11601.1	-58.9	(39, 31)	11935.3	-57.7
(38, 31)	11738.3	+78.3	(39, 32)	12072.4	+79.4
<b>(39, 29)</b>	<b>11660.8</b>	<b>-0.8</b>	(40, 29)	11875.7	-117.3
(39, 30)	11798.0	+138	<b>(40, 30)</b>	<b>11994.9</b>	<b>+1.9</b>
(40, 27)	11583.4	-76.6	(41, 28)	11917.5	-75.5
(40, 28)	11720.6	+60.6	(41, 29)	12054.7	+61.7
(41, 26)	11643.1	-16.9	(42, 27)	11977.2	-15.8
(41, 27)	11780.3	+120.3	(42, 28)	12114.4	+121.4
(42, 24)	11565.6	-94.4	(43, 25)	11899.7	-93.3
(42, 25)	11702.8	+42.8	(43, 26)	12036.9	+43.9
(43, 23)	11625.4	-34.6	(44, 24)	11959.5	-33.5
(43, 24)	11762.6	+102.3	(44, 25)	12096.7	+103.7
(44, 21)	11547.9	-112.1	(45, 22)	11882.0	-111
(44, 22)	11685.1	+25.1	(45, 23)	12019.2	+26.2
(45, 20)	11607.7	-52.3	(46, 21)	11941.9	-51.1
(45, 21)	11744.9	+84.9	(46, 22)	12078.9	+85.9

nanocluster synthesis, two primary stages include (a) the reduction of Au(III) to Au(I) by HSR and (b) the conversion of Au(I) to  $\text{Au}_n(\text{SR})_m$  clusters by reduction with  $\text{NaBH}_4$ . Factors that are important for  $\text{Au}_n$  size control with  $n = 20$ , 24, 39 and 40 include (a) the stirring speed of the reaction mixture, (b) the addition speed of  $\text{NaBH}_4$ , and (c) the amount of  $\text{NaBH}_4$  added (*vide infra*).

#### Stirring speed and effect on cluster size

We found the stirring speed is quite important for controlling the size and monodispersity of gold clusters. As listed in Table 2, during stage I, the stationary condition favors the formation of  $\text{Au}_{20}(\text{SR})_{16}$  nanoclusters, while slow stirring (50 to 100 rpm) favors the formation of  $\text{Au}_{24}(\text{SR})_{20}$ ,  $\text{Au}_{39}(\text{SR})_{29}$ , and  $\text{Au}_{40}(\text{SR})_{30}$ .

During stage II (the reduction of Au(I) by  $\text{NaBH}_4$ ), the stirring speed is even critical for the selective formation of  $\text{Au}_{20}$ ,  $\text{Au}_{24}$ , or  $\text{Au}_{39/40}$ . A slow stirring (approximately 50 rpm) during stage II favors the formation of  $\text{Au}_{20}(\text{SC}_2\text{H}_4\text{Ph})_{16}$ , while a slightly higher speed of stirring (approximately 100 rpm) favored the formation of  $\text{Au}_{24}(\text{SC}_2\text{H}_4\text{Ph})_{20}$ , and with further increased speed to approximately 400 rpm, we

**Table 2 The respective conditions for the syntheses of Au<sub>20</sub>, Au<sub>24</sub>, and mixed Au<sub>39/40</sub>**

Cluster size	Stage I	Stage II	Amount of NaBH <sub>4</sub> (concentration, 0.44 M) per mole of gold and speed of addition	Aging time
	Stirring speed at the stage of Au(III) reduction to Au(I) by 3X HSC <sub>2</sub> H <sub>4</sub> Ph	Stirring speed at the stage of Au(I) reduction to clusters by NaBH <sub>4</sub>		
1 Au <sub>20</sub>	Stationary	Approximately 50 rpm	1 mL (1x), dropwise added over a 30-min period	Approximately 6 hrs
2 Au <sub>24</sub>	50 to 100 rpm	Approximately 100 rpm	1 mL (1x), dropwise added over a 15-min period	Overnight
3 Au <sub>39/40</sub>	50 to 100 rpm	Approximately 400 rpm	1 mL (1x), dropwise added over a 15-min period	Overnight
4 Au <sub>25</sub>	50 to 100 rpm	50 to 400 rpm	5 mL (5x), Dropwise added over a 50-min period	Overnight

obtained new clusters of Au<sub>39</sub>(SC<sub>2</sub>H<sub>4</sub>Ph)<sub>29</sub> and Au<sub>40</sub>(SC<sub>2</sub>H<sub>4</sub>Ph)<sub>30</sub>. This controlled reaction process for tuning cluster size is quite interesting. We believe that the aggregated Au(I)SR species are broken into small fragments upon reduction or partial reduction by NaBH<sub>4</sub>. Different stirring speed for stage II would influence the kinetics of the reduction reaction of Au(I)SR, and the different stirring speeds also give rise to different sheering forces that would break polymeric Au(I)SR into different sized fragments; such different sized fragments seem to subsequently grow into different sized clusters based upon our results.

Regarding the aggregated Au(I)SC<sub>2</sub>H<sub>4</sub>Ph species in the solution, structural characterization (e.g., by NMR or X-ray diffraction) is still difficult to carry out as the Au(I) intermediate species is poorly soluble in common solvents. Thermal gravimetric analysis determined the composition of Au(I):SR to be 1:1, but the aggregation degree (e.g., how many repeat units in [Au(I)SC<sub>2</sub>H<sub>4</sub>Ph]<sub>x</sub>) and what structures [Au(I)SC<sub>2</sub>H<sub>4</sub>Ph]<sub>x</sub> may adopt are all unknown yet. Possible structures of [Au(I)SC<sub>2</sub>H<sub>4</sub>Ph]<sub>x</sub> include linear chains, ring [53–57], or lamellar structures. The characterization of Au(I)SR still need major efforts in future work.

#### Dropwise addition speed of NaBH<sub>4</sub> and effect on cluster size

In addition to the stirring speed during stage II, the addition speed of NaBH<sub>4</sub> (aqueous solution) to reduce Au(I) into clusters also plays an important role in controlling the final cluster size. We have tested that, in the synthesis of Au<sub>20</sub>(SC<sub>2</sub>H<sub>4</sub>Ph)<sub>16</sub>, if the initial drops of NaBH<sub>4</sub> solution (0.44 mol/L, 1 mL) were added rapidly, the light yellow solution of Au(I) aggregates would rapidly become brown or deep black, and the product would contain more Au<sub>24</sub> and Au<sub>39/40</sub> clusters, instead of the predominant Au<sub>20</sub> as the case of very slow addition of NaBH<sub>4</sub> (over a period of approximately 30 min) (entry 1, Table 2). After optimization, we found that adding NaBH<sub>4</sub> (0.44 mol/L, 1 mL, same concentration and amount as the Au<sub>20</sub> synthesis) over a period of

approximately 15 min gave rise to predominant Au<sub>24</sub> (under approximately 100 rpm stirring condition) or Au<sub>39/40</sub> (under approximately 400 rpm stirring condition); see entries 2 and 3 of Table 2. Thus, controlled reduction of Au(I) is very important for size selective formation of Au<sub>20</sub>, Au<sub>24</sub>, or Au<sub>39/40</sub>. The selective formation of Au<sub>39/40</sub> over Au<sub>24</sub> - which differ only in the stirring speed during stage II (i.e., 400 vs 100 rpm, Table 2) - should be due to the different reaction kinetics in the reduction process of Au(I) species into clusters. In a recent synthetical work on gold/phosphine nanocluster synthesis, Pettibone and Hudgens identified a growth-etching cyclic process that occurs around the most stable cluster species to form monodisperse product [4,58,59]. This size selective growth mechanism provides important information on the gold/phosphine system. The reaction kinetics of the gold/thiol system, however, still needs significant input in order to unravel the details of the kinetic process. Mass spectrometric monitoring of the reaction intermediates would provide valuable information and should be pursued in future work.

#### Degree of reduction of Au(I) and effect on cluster size

With respect to the growth of Au<sub>20</sub>, Au<sub>24</sub>, and Au<sub>39/40</sub> nanoclusters, an interesting question arises naturally: why the ubiquitous Au<sub>25</sub> nanocluster is not formed under these conditions (entries 1 to 3, Table 2). The synthesis of Au<sub>25</sub>(SC<sub>2</sub>H<sub>4</sub>Ph)<sub>18</sub> is typically done under experimental conditions of fast stirring and rapid reduction of Au(I) with large excess of NaBH<sub>4</sub> (approximately 10 equivalents (eq) of NaBH<sub>4</sub> per mole of gold). An important difference lies in that the syntheses of Au<sub>20</sub>, Au<sub>24</sub>, and Au<sub>39/40</sub> clusters all involve 1 eq of NaBH<sub>4</sub> per gold, i.e., 1 mL of NaBH<sub>4</sub> solution (0.44 mol/L), Table 2. This implies that the degree of reduction of Au(I) might affect the cluster size, and the formation of Au<sub>25</sub> clusters might necessitate over reduction of Au(I) with a large excess of NaBH<sub>4</sub>.

To find out whether the reduction degree of Au(I) species affect the final cluster size, we adopt the same

stirring conditions as the synthesis of  $\text{Au}_{24}$  and  $\text{Au}_{39/40}$  (see entry 4, Table 2), but we add more  $\text{NaBH}_4$  (e.g., 5 eq, rather than 1 eq for the synthesis of  $\text{Au}_{24}$  and  $\text{Au}_{39/40}$ ). The addition speed of  $\text{NaBH}_4$  solution is kept comparable to the syntheses of  $\text{Au}_{24}$  and  $\text{Au}_{39/40}$  clusters. Interestingly, dropwise addition of 5 eq of  $\text{NaBH}_4$  does result in selective formation of  $\text{Au}_{25}$ , instead of  $\text{Au}_{24}$  or  $\text{Au}_{39/40}$ , evidenced by its characteristic spectroscopic features (see Figure S2 in Additional file 1). Thus, the growth of  $\text{Au}_{25}$  nanoclusters does require a rich reductant ( $\text{NaBH}_4$ ), as opposed to lean  $\text{NaBH}_4$  for  $\text{Au}_{20}$ ,  $\text{Au}_{24}$ , and  $\text{Au}_{39/40}$  synthesis. The fast stirring and rapid addition of  $\text{NaBH}_4$  seem not the key to the synthesis of  $\text{Au}_{25}$  nanoclusters.

## Conclusions

This work has demonstrated the effectiveness of controlled reduction for synthesizing different sized gold nanoclusters. Specifically, slow stirring and slow addition of 1 eq  $\text{NaBH}_4$ /mol of gold are critical to effect the preferential growth of the series of  $\text{Au}_{20}$ ,  $\text{Au}_{24}$ , and  $\text{Au}_{39/40}$  nanoclusters. In addition to the reaction kinetics, controlling the degree of reduction also leads to different sized nanoclusters, as demonstrated in the selective formation of  $\text{Au}_{25}$  over  $\text{Au}_n$  ( $n = 20, 24, 39/40$ ). Future work is hoped to offer deeper mechanistic understanding of the  $\text{Au(I)}$  formation and the  $\text{Au(I)}$  reduction process by  $\text{NaBH}_4$ . Mechanistic understanding of the cluster growth process will eventually permit high yielding synthesis of a full series of monodisperse gold nanoclusters.

## Additional file

**Additional file 1: Mass spectrum in the range of  $m/z$  2,000 to 8,000 and comparison of the UV-vis spectrum.** Figure S1 shows the ESI mass spectrum in the range of  $m/z$  2,000 to 8,000. Residual  $\text{Au}_{24}(\text{SC}_2\text{H}_4\text{Ph})_{20}$  clusters (in mono-Cs adducts) were observed at  $m/z$  7603. The low mass portion contains all  $(\text{CsAc})_n\text{Cs}^+$  signals with equal spacing of 191.9 ( $=\text{CsAc}$ ), for example, the  $m/z$  2,051.99 is assigned to  $(\text{CsAc})_{10}\text{Cs}^+$ . Figure S2 shows the comparison of the UV-vis spectrum of the crude products (profile a) and of the purified  $\text{Au}_{25}(\text{SC}_2\text{H}_4\text{Ph})_{18}$  nanoclusters (profile b).

## Abbreviations

$\text{NaBH}_4$ : sodium borohydride; TOAB: tetraoctylammonium bromide.

## Competing interests

The authors declare that they have no competing interests.

## Authors' contributions

XM and ZL participated in all the studies and in writing this paper. MZ and RJ supervised in the concept of the study and participated in its design and in the revision of the manuscript. All authors read and approved the final manuscript.

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